

$\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ Ternary Skutterudites: Processing and Thermoelectric Properties

Jon Mackey

Mechanical Engineering,
University of Akron

Alp Sehirlioglu

Materials Science and Engineering,
Case Western Reserve University

Fred Dynys

NASA Glenn Research Center

NASA Cooperative Agreement: NNX08AB43A

NASA/USRA Contract: 04555-004



Introduction

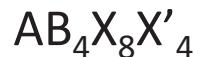
Processing

Properties

Objectives

- Investigate ternary skutterudite systems
- Focus on finding a p-type skutterudite with improved ZT
- Study behavior of the skutterudite $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$

Ternary SKD Systems



A={La,Ce,Nb,Yb,Ca,...}

B={Fe,Co,Ni,Rh,Ir,...}

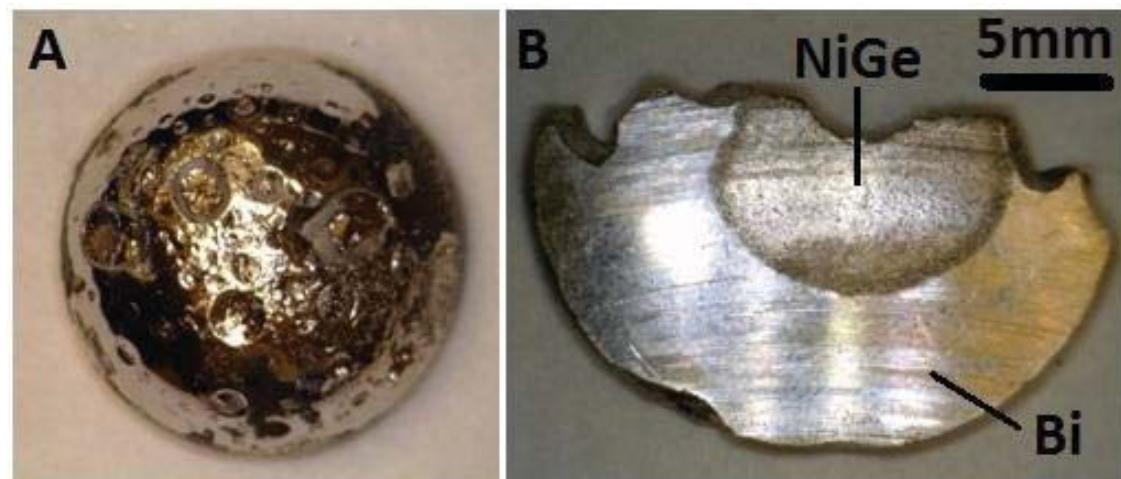
X={P,As,Sb,Bi}

X'={Ge,Sn}

Bauer et. al Acta Phys. Polon. B 34 (2003).

Systems Investigated

- Ternary systems studied with combination of solidification and powder processing techniques
- $\text{Ni}_4\text{Bi}_8\text{Ge}_4$
 - Shown below, skutterudite phase was not obtained
- $\text{Ni}_4\text{Sb}_8\text{Ge}_4$
 - Skutterudite phase not obtained
- $\text{Ni}_4\text{Sb}_8\text{Sn}_4$



Objectives

- Investigate ternary skutterudite systems
- Focus on finding a p-type skutterudite with improved properties
- Study behavior of the skutterudite $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$

Ternary SKD Systems

AB_4X_{12}
 $\text{AB}_4\text{X}_8\text{X}'_4$
 $\text{A}=\{\text{La}, \text{Ce}, \text{Nb}, \text{Yb}, \text{Ca}\}$
 $\text{B}=\{\text{Fe}, \text{Co}, \text{Ni}, \text{Rh}, \text{In}\}$
 $\text{X}=\{\text{P}, \text{As}, \text{Sb}, \text{Bi}\}$
 $\text{X}'=\{\text{Ge}, \text{Sn}\}$

Bauer et. al Acta Phys. Polon. B 34 (2003).

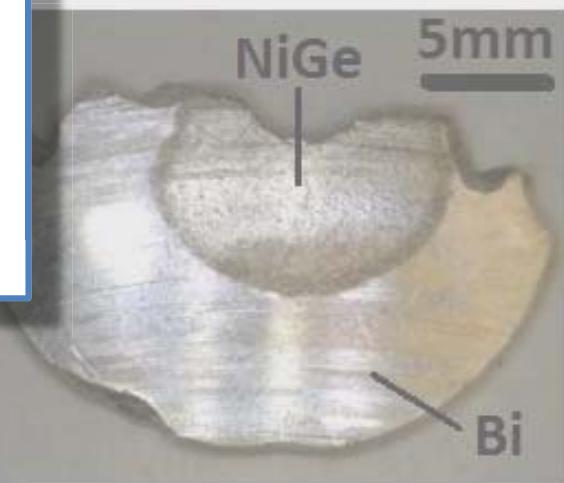
Systems Investigated

- Ternary systems studied with combination of solidification and powder processing

$\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$

- Grytsiv et. al has reported a $\text{Ni}_4\text{Sb}_8\text{Sn}_4$ skutterudite system
- Interested in obtaining p-type behavior
- Parameters of study:
 - $x = \{0, 0.5, 1, 1.5, 2\}$
 - $y = \{4, 5\}$
- Samples created from a melt/mill/hot press procedure

Grytsiv et. al J. Phys.: Condens. Matter 14 (2002).



Introduction

Processing

Properties

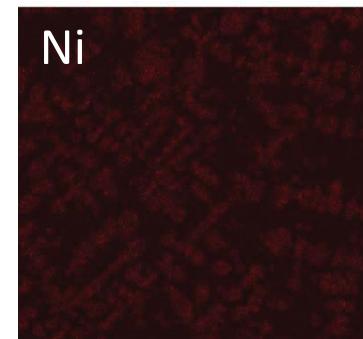
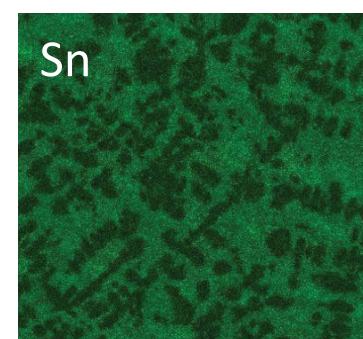
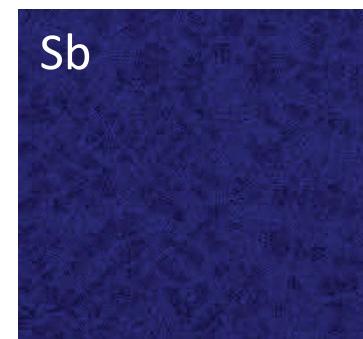
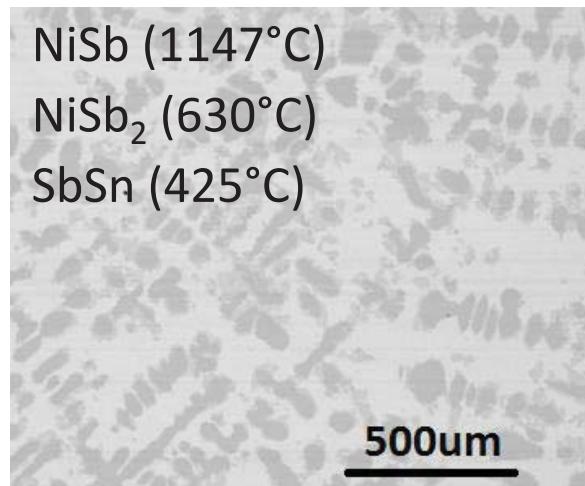
ICP analysis of an ingot

- 2 Hr @ 1100°C (+20,-10°C /min)
- Silica crucible in He atmosphere
- <1% wt loss



Target	X	X	X	
Co	9.4	9.1	7.3	9.0
Ni	15.6	14.9	13.7	14.6
Sb	43.7	42.4	43.7	44.1
Sn	31.2	33.5	35.3	32.2
Ca	0	2e-4	7e-4	7e-4
Mg	0	1e-4	2e-4	2e-4
Na	0	3e-3	4e-3	4e-3

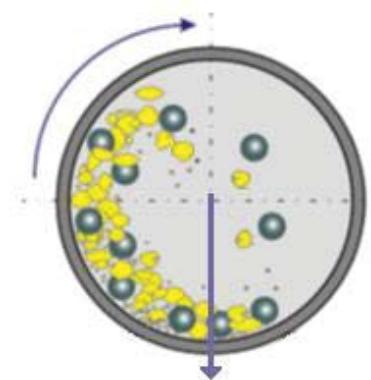
EDS map of an ingot



Introduction

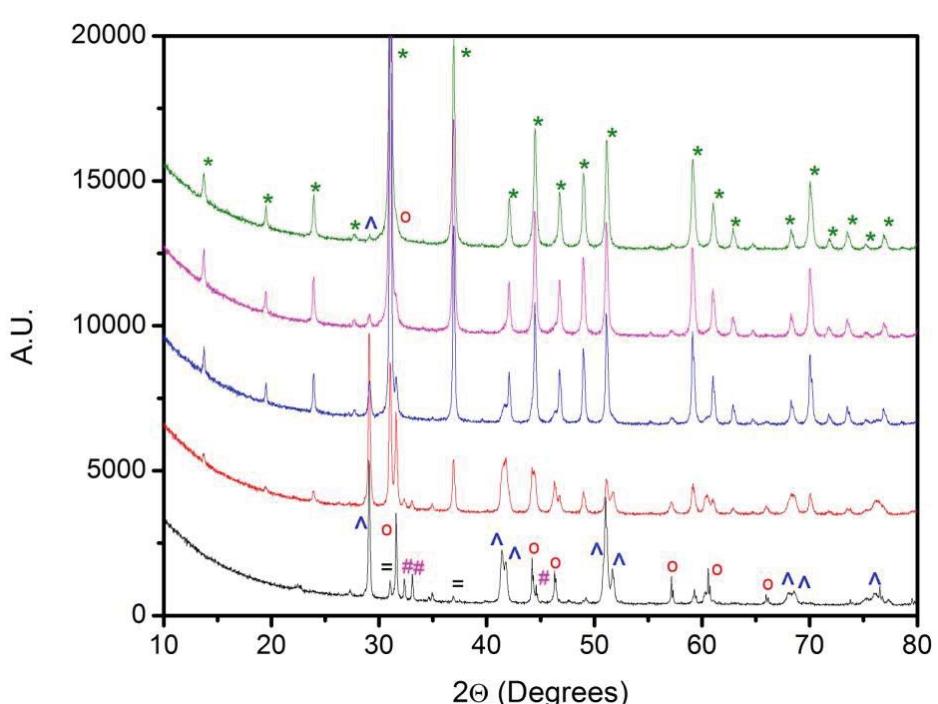
Processing

Properties



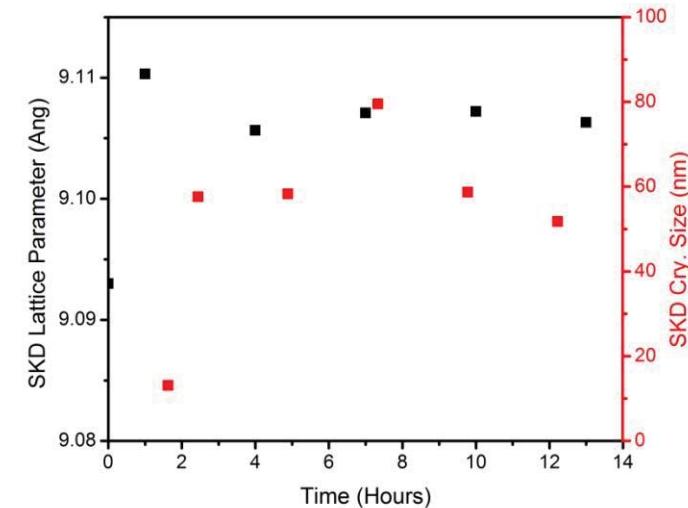
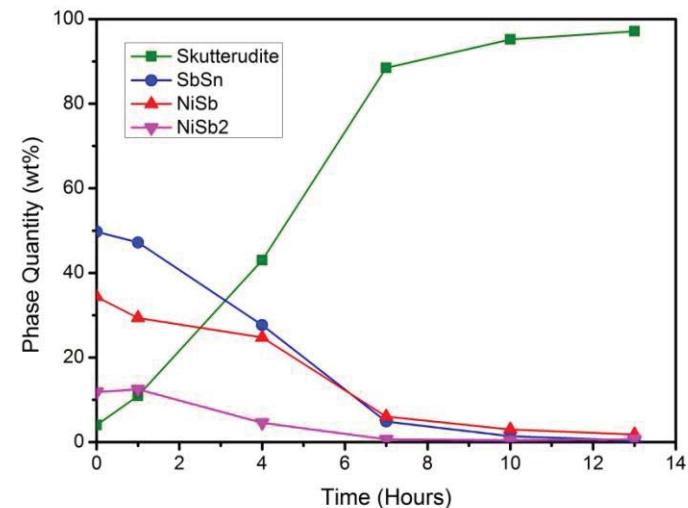
Milling Details

- Ingots crushed by hand
- Planetary mill
 - 550 rpm
 - Ball to powder weight ratio 3.8
 - Ar atmosphere



Co_xNi_{4-x}Sb_{12-y}Sn_y Ternary Skutterudites

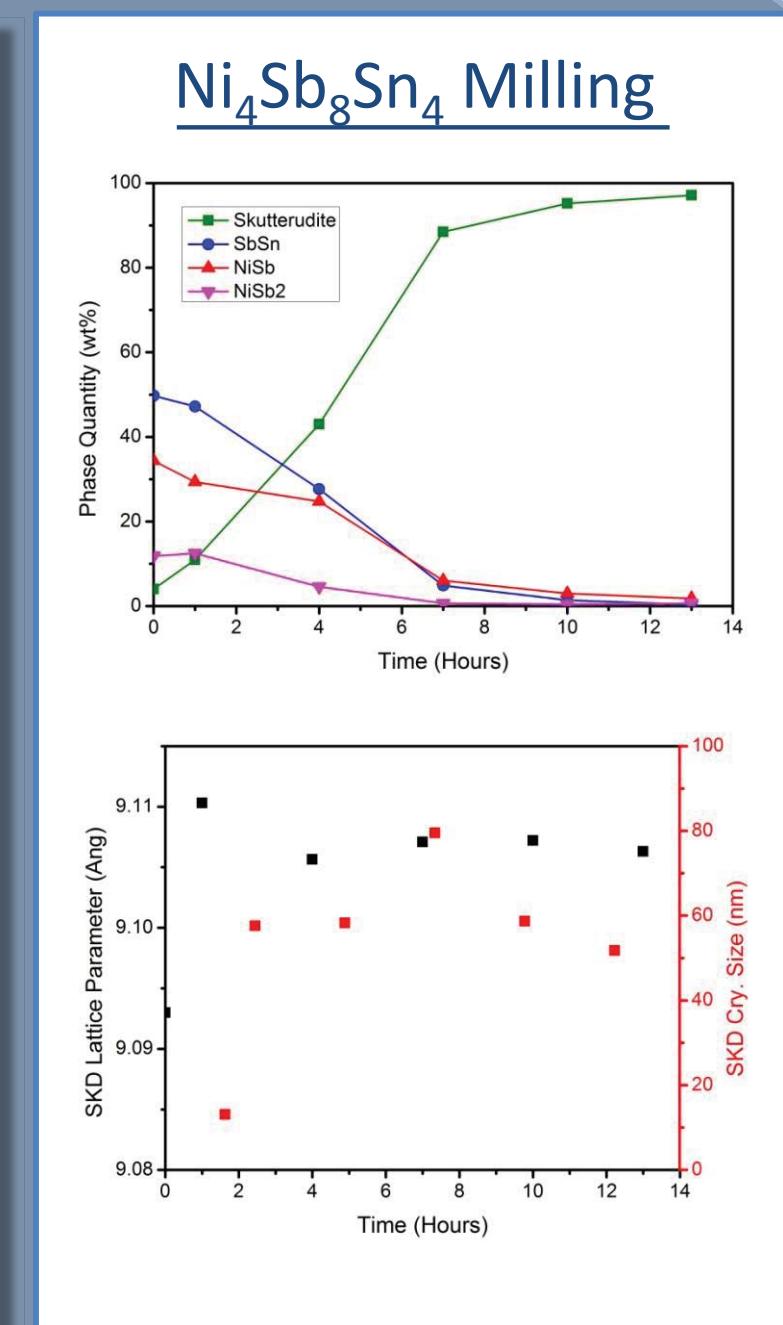
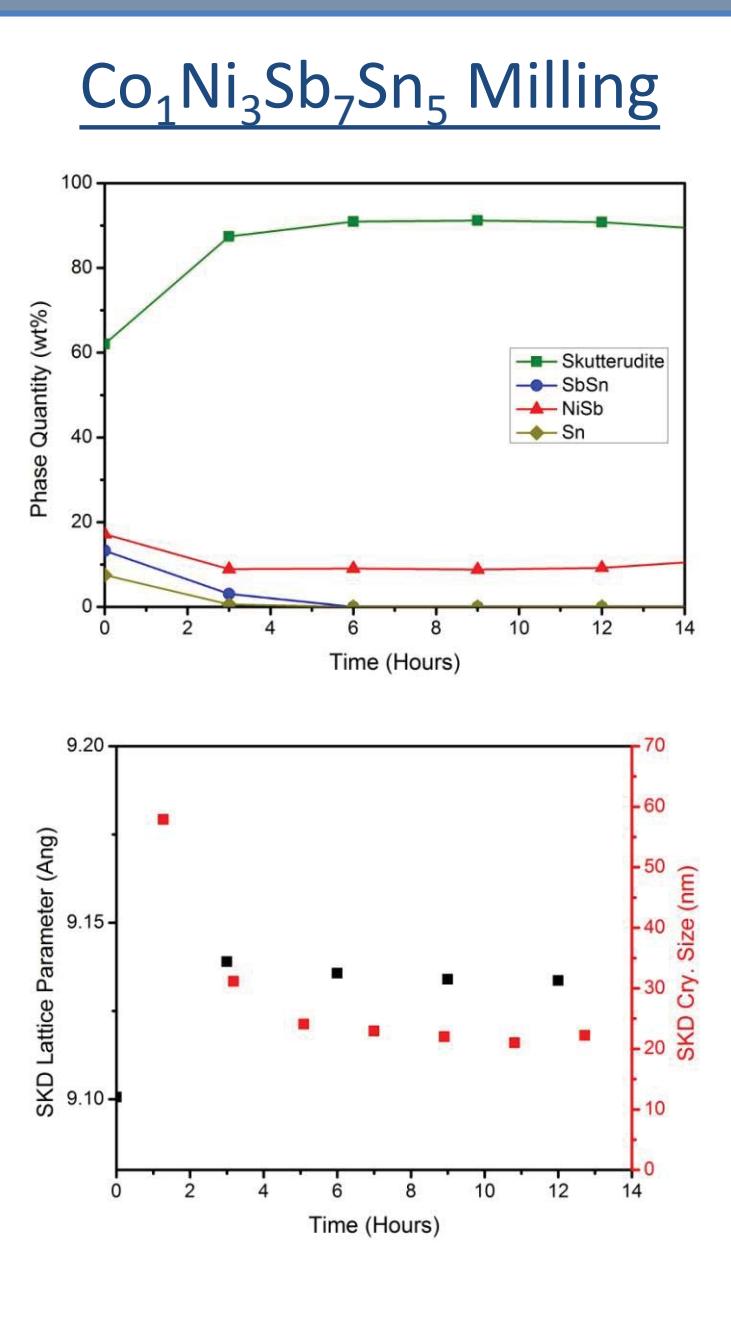
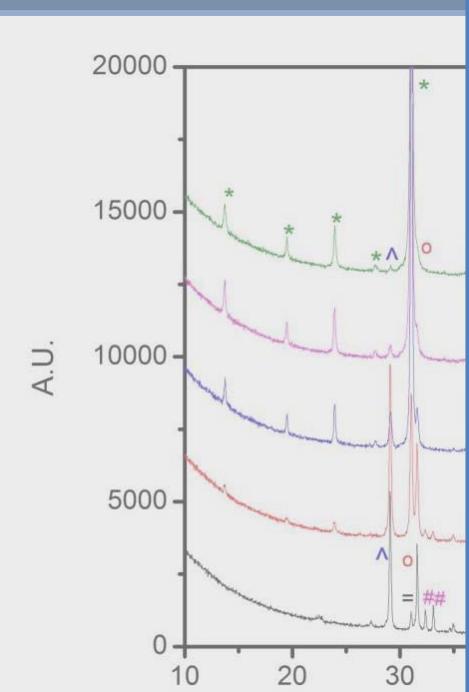
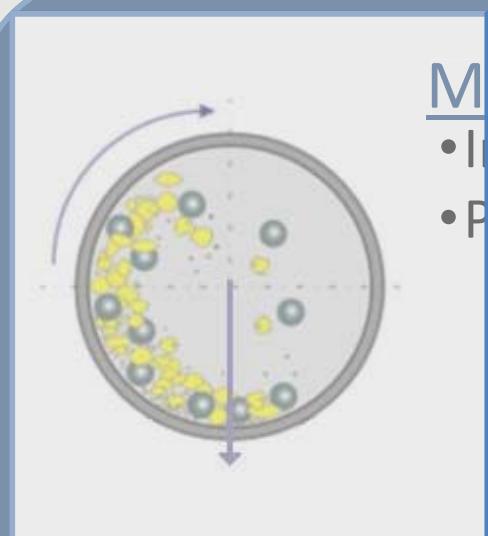
Ni₄Sb₈Sn₄ Milling



Introduction

Processing

Properties



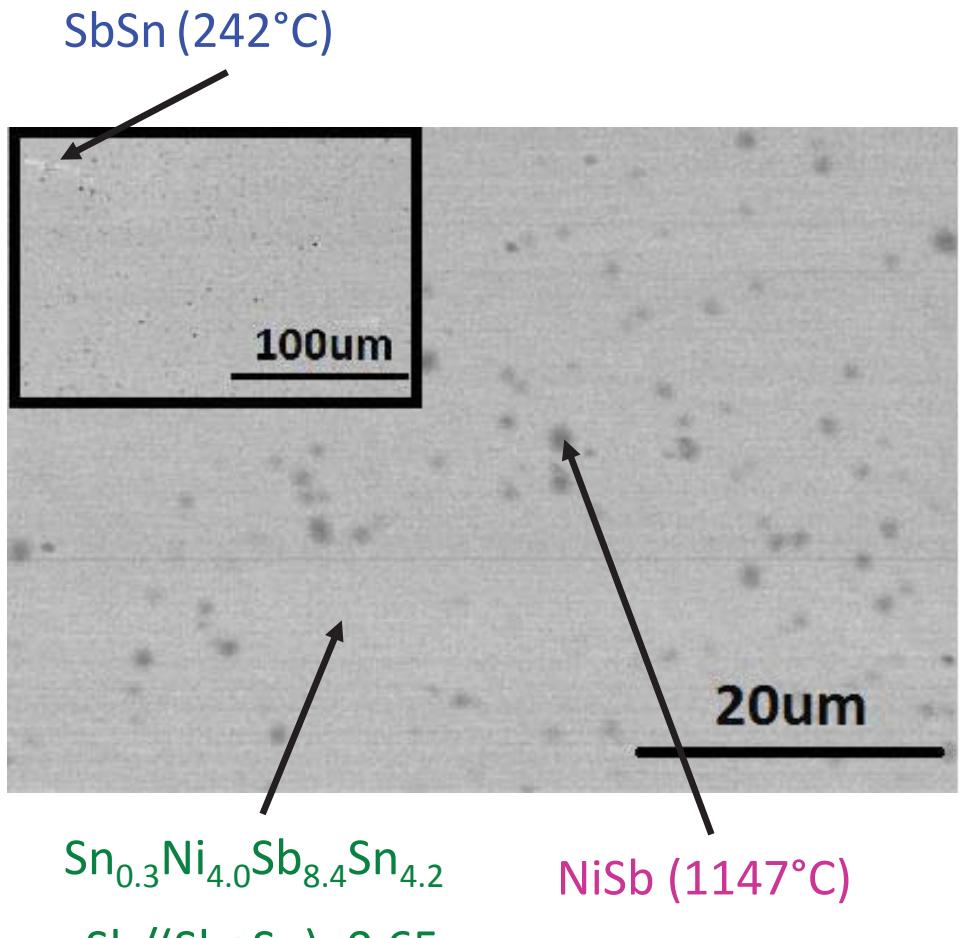
Introduction

Processing

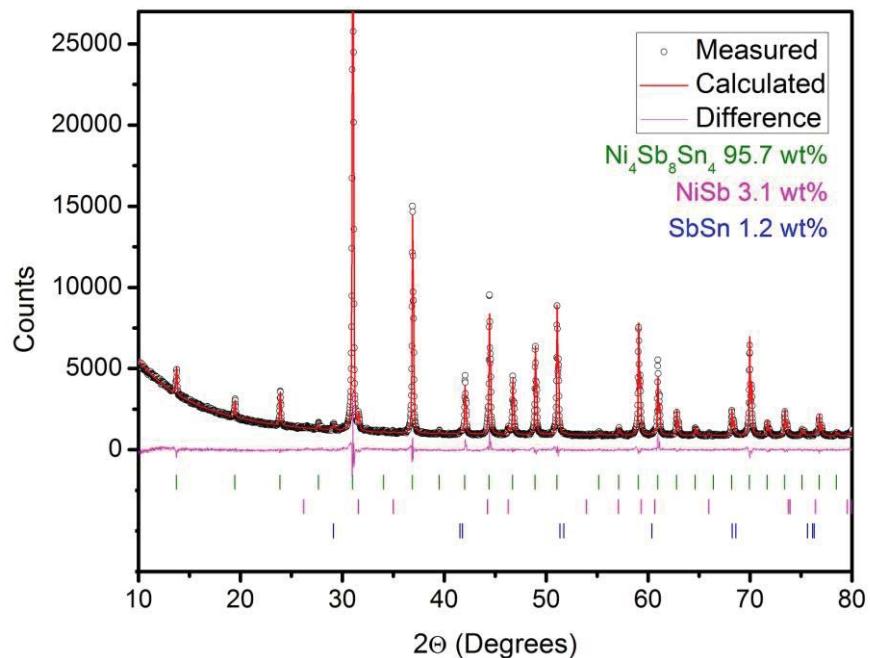
Properties

SEM/EPMA on Hot Pressed

Nominal Composition $\text{Ni}_4\text{Sb}_8\text{Sn}_4$



Rietveld on Hot Pressed



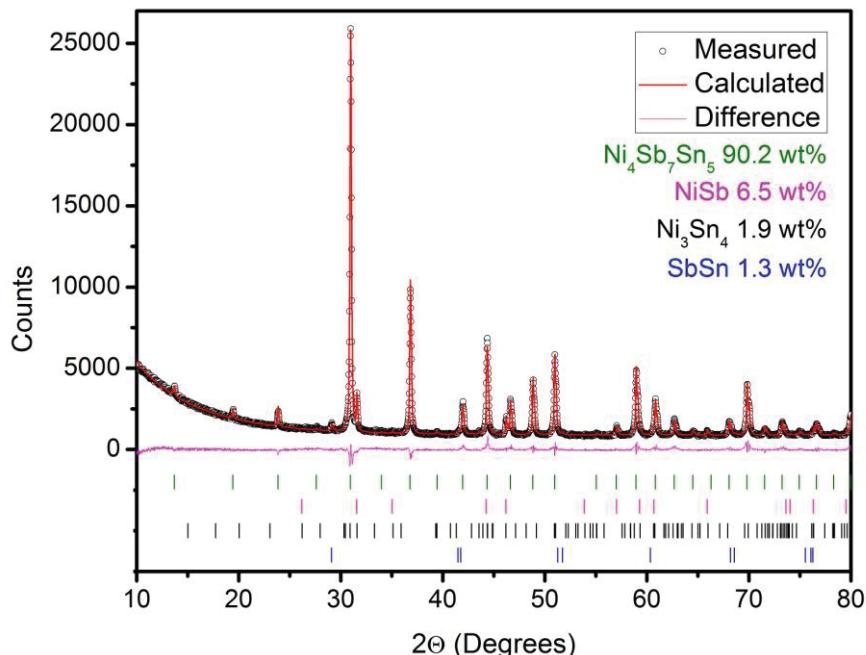
Parameter	Value
GOF	1.78
Lattice (Å)	9.115
Y	0.158
Z	0.336
2a Occ. (Sn)	0.27
24g Occ. (Sb+Sn)	0.99

Introduction

Processing

Properties

Rietveld on Hot Pressed

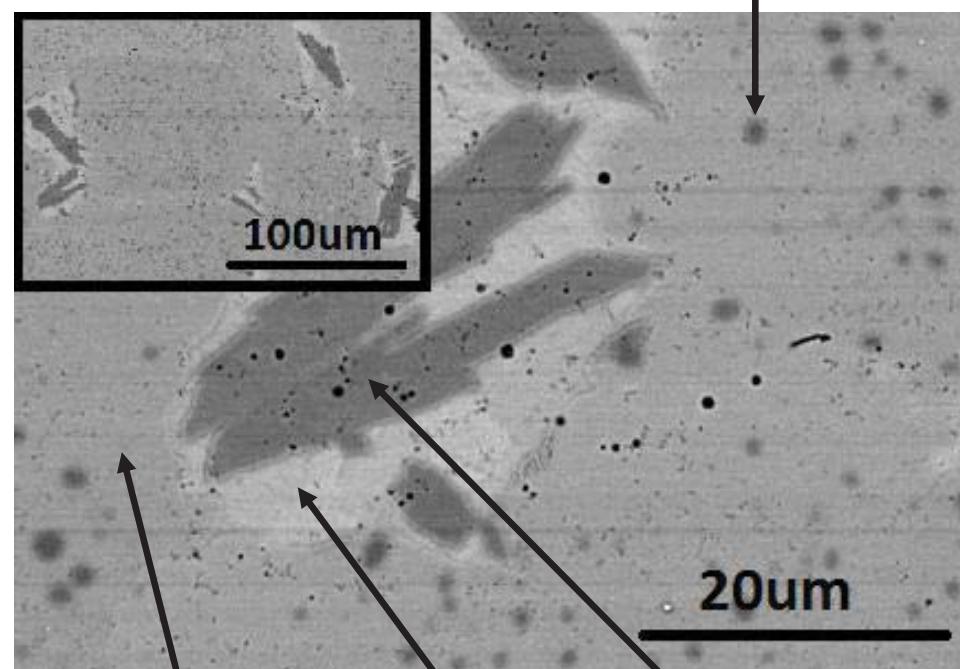


Parameter	$\text{Ni}_4\text{Sb}_7\text{Sn}_5$	$\text{Ni}_4\text{Sb}_8\text{Sn}_4$
GOF	1.67	1.78
Lattice (Å)	9.130	9.115
Y	0.159	0.158
Z	0.336	0.336
2a Occ. (Sn)	0.39	0.27
24g Occ. (Sb+Sn)	0.95	0.99

SEM/EPMA on Hot Pressed

Nominal Composition $\text{Ni}_4\text{Sb}_7\text{Sn}_5$

NiSb (1147°C)

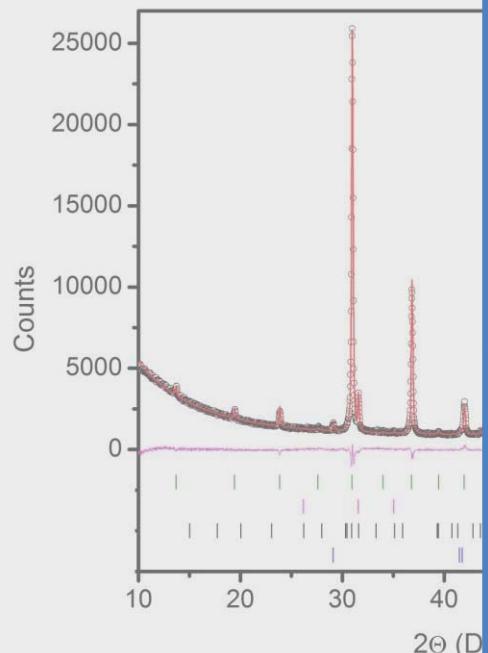


Introduction

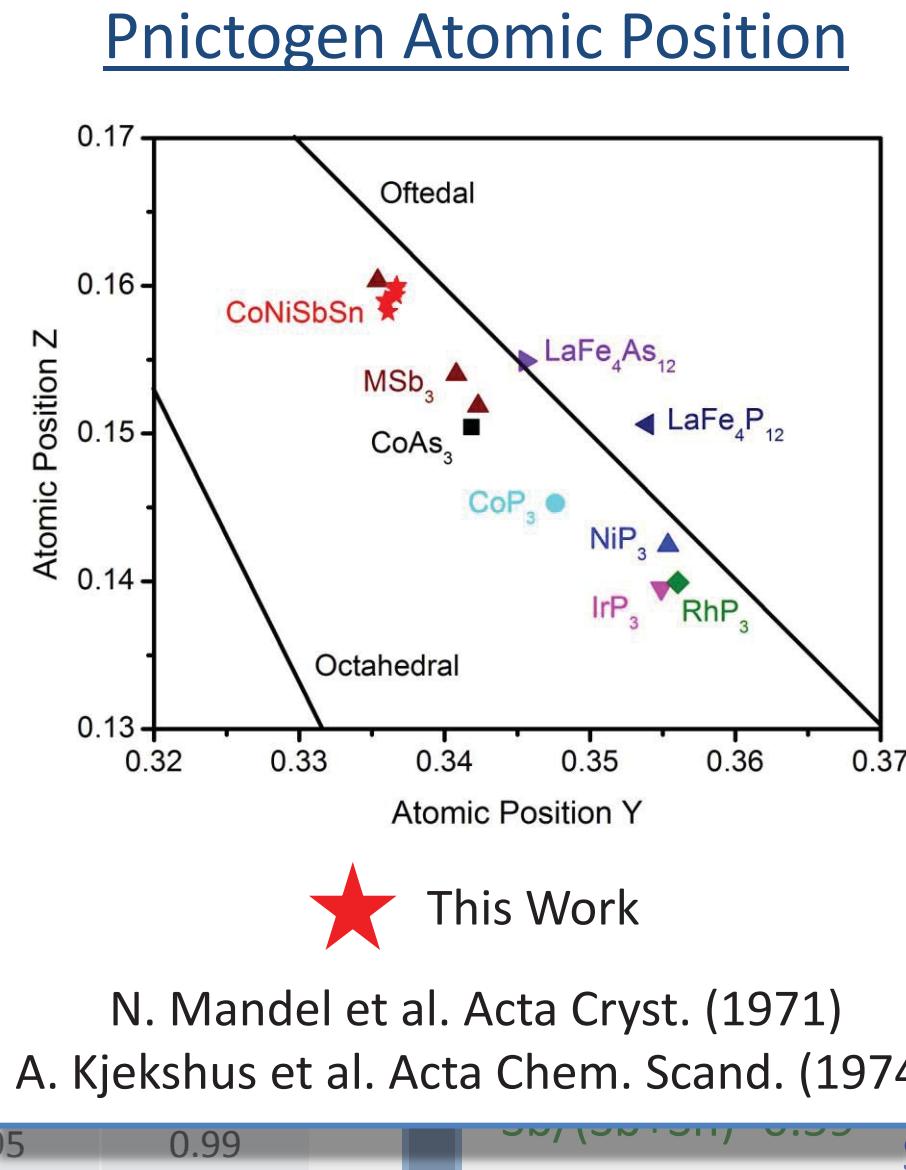
Processing

Properties

Rietveld on He^+ Processed



Parameter	Ni ₄ S
GOF	1.
Lattice (Å)	9.1
Y	0.1
Z	0.3
2a Occ. (Sn)	0.
24g Occ. (Sb+Sn)	0.

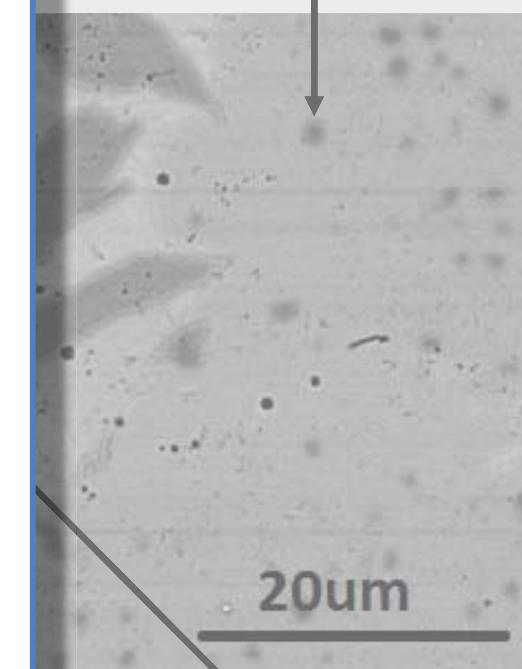


N. Mandel et al. Acta Cryst. (1971)
A. Kjekshus et al. Acta Chem. Scand. (1974)

on Hot Pressed

Position Ni₄Sb₇Sn₅

NiSb (1147°C)



Ni₃Sn₄ (230°C)

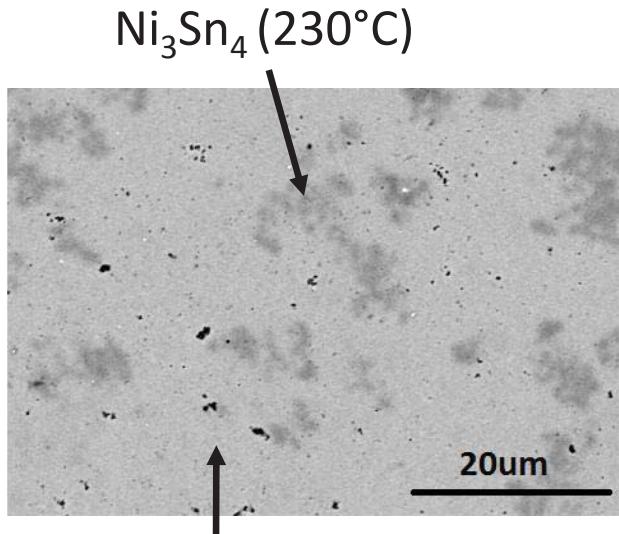
SnSb (242°C)

Introduction

Pressed $\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$

Density 7.64 g/cm³

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	82.6
Ni_3Sn_4	8.7
Sn	6.2

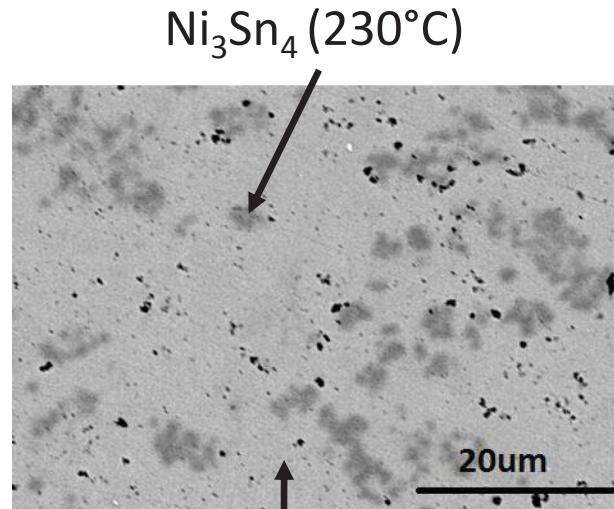


Processing

200°C Anneal 72 Hrs

Density 7.25 g/cm³

Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	80.0
Ni_3Sn_4	11.9
Sn	7.6

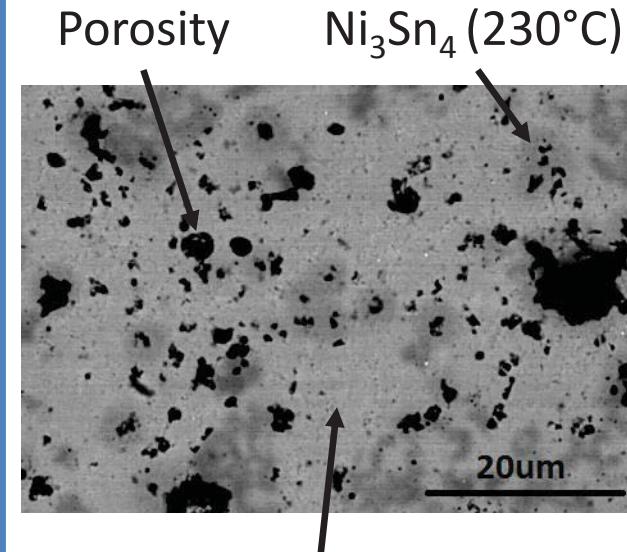


Properties

400°C Anneal 72 Hrs

Density 6.75 g/cm³

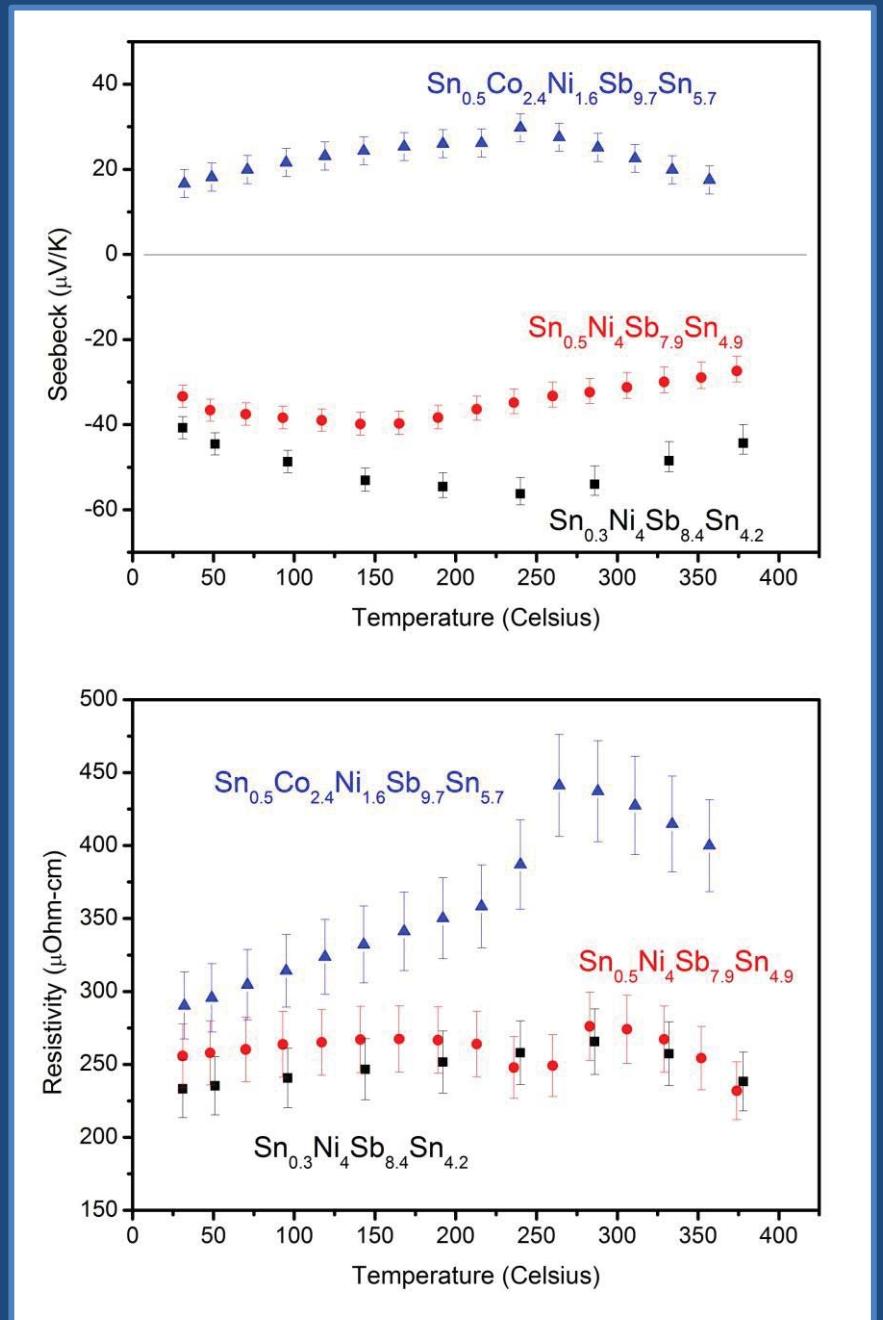
Phase	Wt%
$\text{Co}_2\text{Ni}_2\text{Sb}_7\text{Sn}_5$	73.6
Ni_3Sn_4	14.7
Sn	10.0



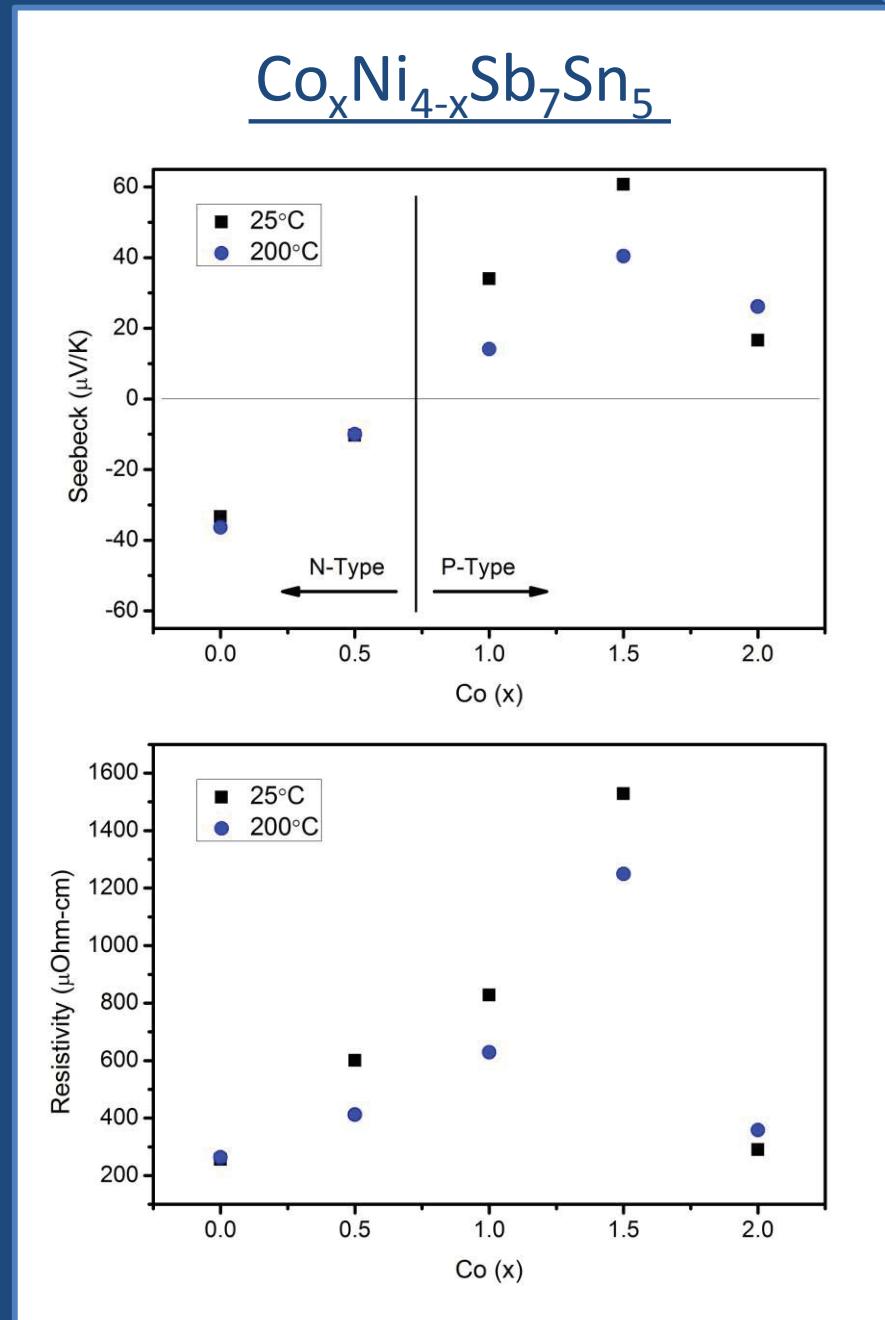
Introduction

Processing

Properties



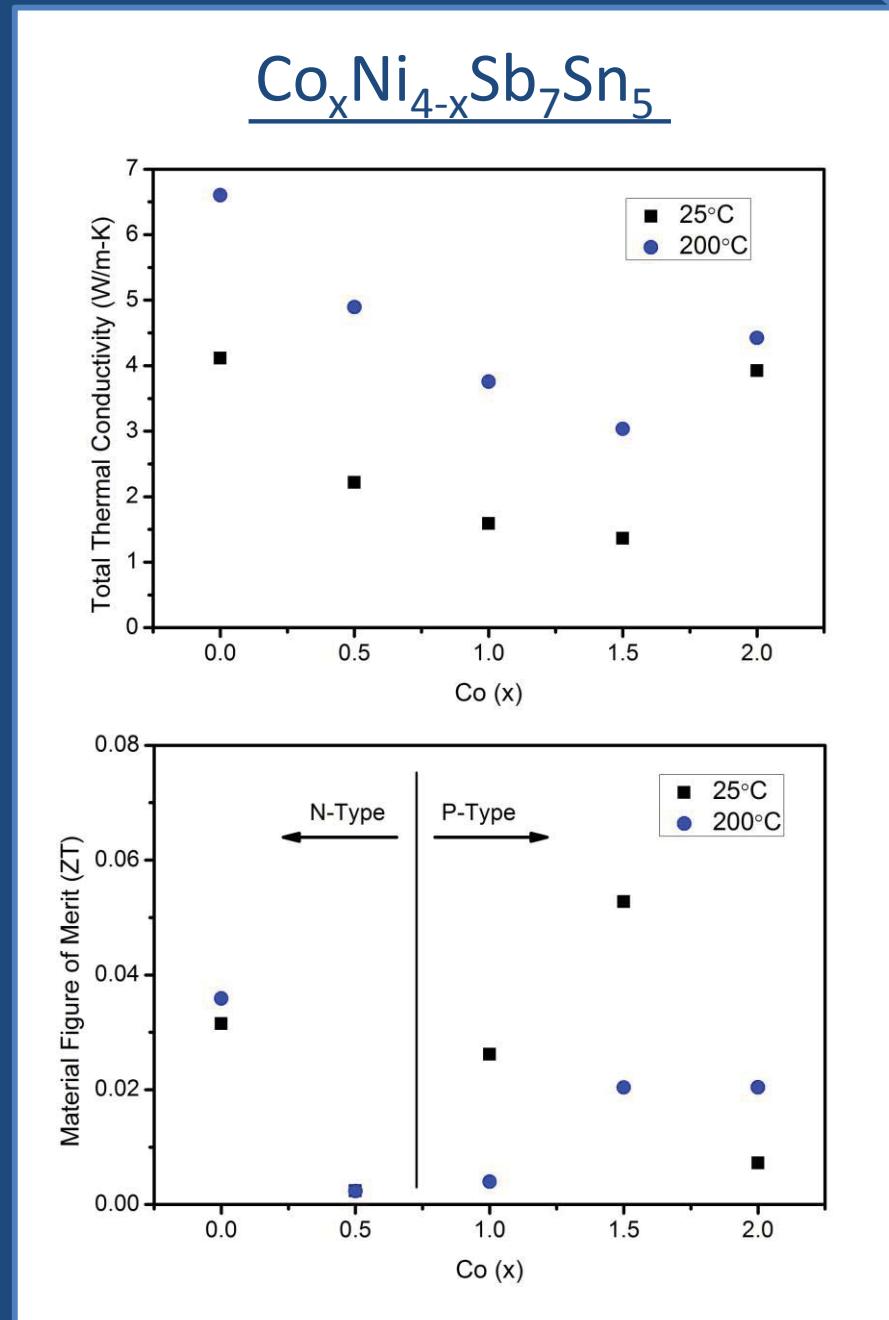
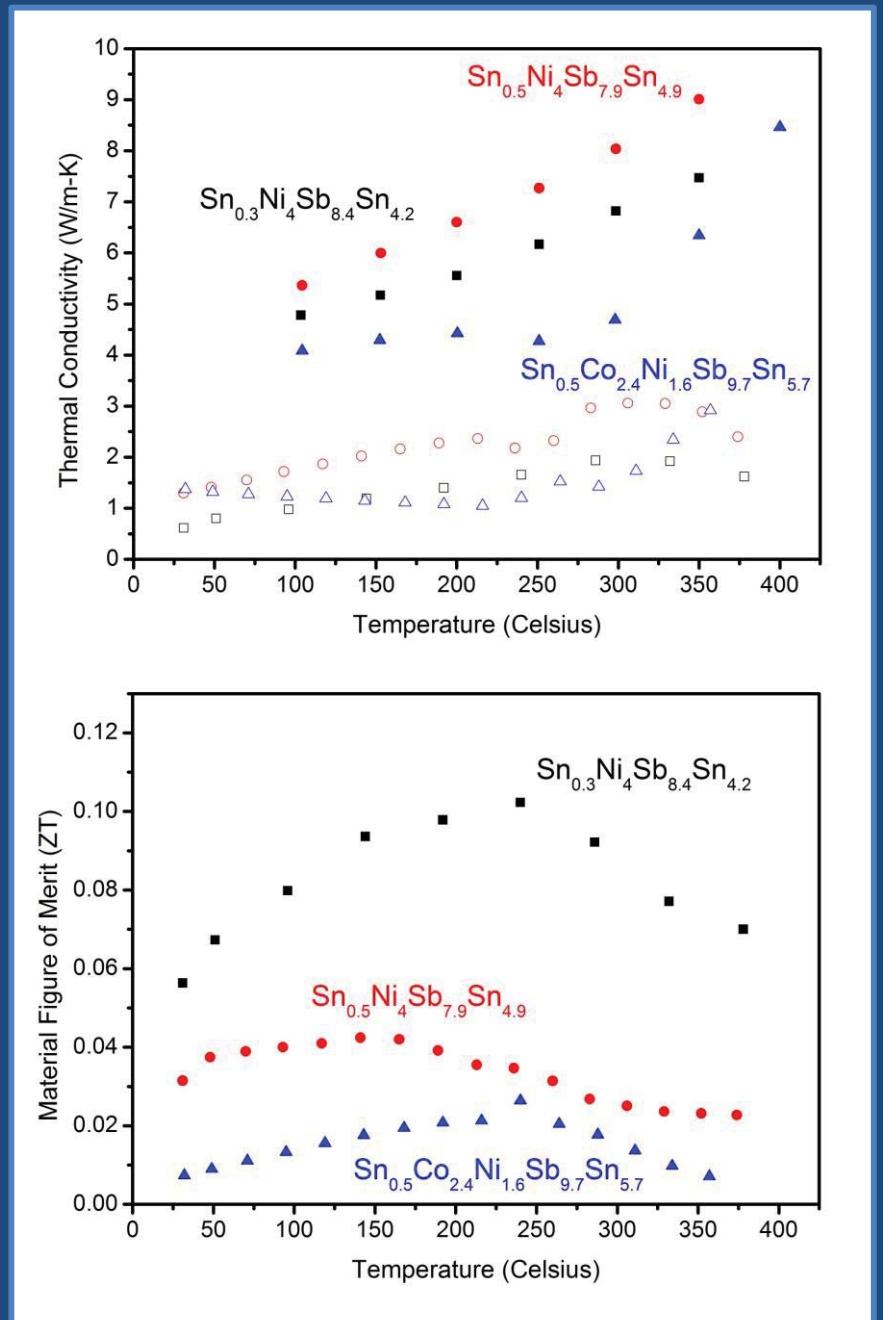
$\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ Ternary Skutterudites



Introduction

Processing

Properties



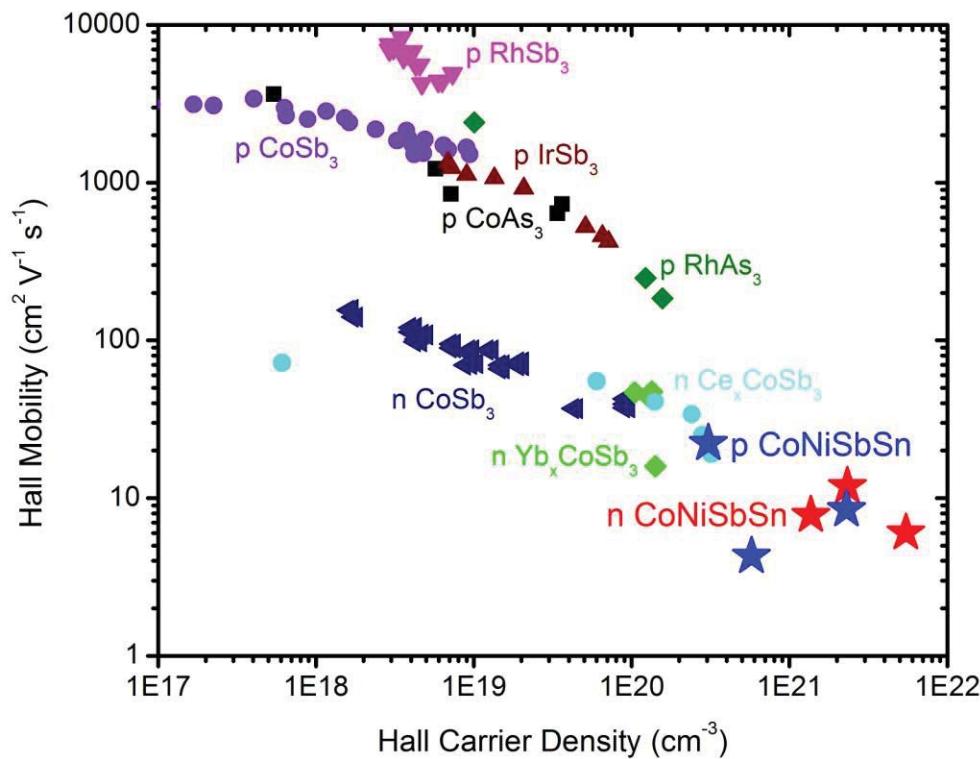
$\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ Ternary Skutterudites

Introduction

Processing

Properties

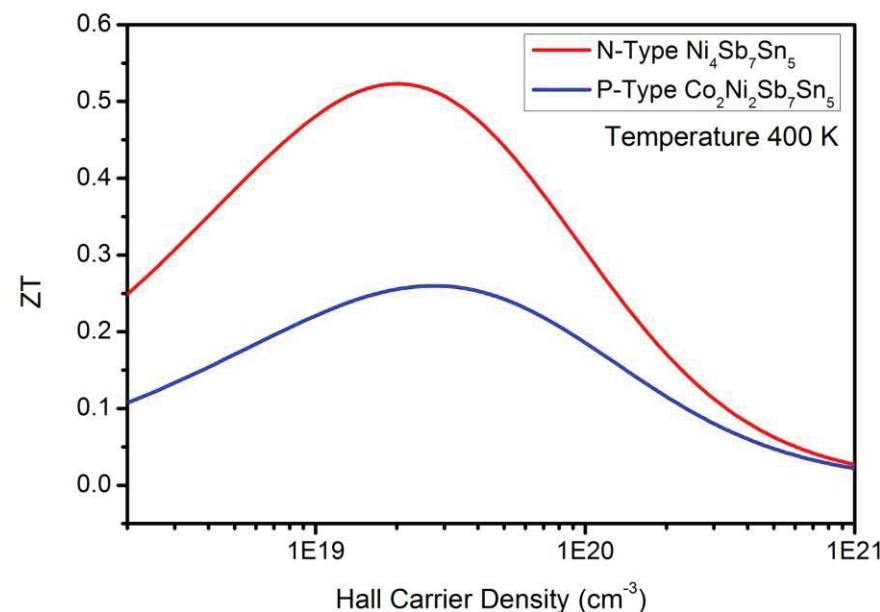
Mobility and Carrier Comparison



Yb_xCoSb_3 : L. Fu et al. *Intermetallics* (2013)
 Ce_xCoSb_3 : D. Morelli et al. *Phys. Rev. B* (1997)
Rest: J.-P. Fleurial et al. *Proc. XVI ICT* (1997)

S.P.B. Modeling

- Applied a single parabolic band model to the system
- Carrier mass (m/m_e)
 - N-Type: 5.48
 - P-Type: 1.48
- Optimal carrier density
 - N-Type: $2.1\text{E}19 \text{ cm}^{-3}$
 - P-Type: $2.7\text{E}19 \text{ cm}^{-3}$



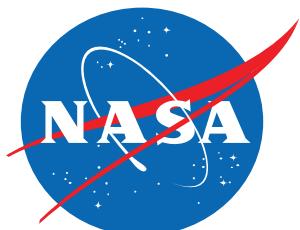
Introduction

Processing

Properties

Conclusion

- The $\text{Co}_x\text{Ni}_{4-x}\text{Sb}_{12-y}\text{Sn}_y$ skutterudite can be synthesized from a melt/mill/hot press schedule
- Both n- and p-type conduction can be achieved by Co doping
- System exhibits low thermal conductivity, but also low Seebeck coefficient
- Thermoelectric performance of the system is hindered by large carrier densities and low carrier mobilities



The
of University
Akron

CASE WESTERN RESERVE
UNIVERSITY EST. 1826
think beyond the possible®

Acknowledgements

Tom Sabo, Ray Babuder, Ben Kowalski, Clayton Cross, Kerem Sayir

NASA Glenn Research Center

Dr. Sabah Bux, Dr. Jean-Pierre Fleurial
JPL

NASA Cooperative Agreement:
NNX08AB43A

NASA/USRA Contract:
04555-004